MS35 O3

The Effect of Graft Copolymers on Calcium Oxalate Crystallization Semra Kırboğa, Emel Akyol, Özlem Doğan, Mualla Öner *Yıldız Technical University, Chemical Engineering Department, Davutpasa 34210 Istanbul, Turkey*. E-mail: oner@yildiz.edu.tr

Keywords: calcium oxalate, crystallization, polymeric additives

The control of crystal growth and morphology of crystal is considerable importance in industrial crystallization and biomineralization. The formation of scales which is affected by temperature, stirring and supersaturation, reduce the heat transfer efficiency of the evaporation process leading to increased energy consumption and losses in production time. The removal of these scales is not only costly but also time consuming because of the tenacious nature of the scales. So, by using polymeric additives it is possible to overcome these industrial problems. In this study, the effects of polyethyleneglycol methacrylate-co-vinylsulfonic acid graft copolymers and vinylsulfonic acid homopolymer additives on the crystallization of calcium oxalate monohydarate have been investigated at different temperatures. Calcium oxalate (CaOx) crystals with different morphologies and phase structures were prepared by precipitation reaction of sodium oxalate with calcium chloride in the absence and presence of polymeric additives. The effect of polymers on the rate of precipitation of calcium oxalate has been determined by recording the decrease of solution conductivity as a function of time. Addition of vinylsulfonic acid homopolymer in a CaOx crystallization system promoted the formation of COD (calcium oxalate dihydrate) respectively, graft copolymers and homopolymer modified the crystal size of COM and COD, the extent of which was dependent on the concentrations of polymeric additives. .

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Reaction phase diagram of pseudo four components Li-Ni-Co-Ti oxides by combinatorial technology

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Keywords: Combinatorial material science, Electrostatic spray deposition, Electrode materials, Reaction phase diagram, Powder X-ray diffraction

Recently, the exploration of new functional materials increasingly pursues multi-element structures. Therefore, investigation of the synthesis condition increases, and sample preparation by conventional methods is very time-consuming. As an example, many researchers studying for electrode materials also spend much time for exploring pseudo three- or four-component compounds such as $Li(Ni_{0.5},Co_{0.5})O_2$, $Li(Ni_{0.33}Co_{0.33}Mn_{0.33})O_2$ and so on.
Combinatorial technology is promising way for exploring new functional materials. We have hitherto developed high-throughput materials exploration system. In this study, we have explored the new layered-type pseudo four-components Li-Ni-Co-Ti oxides by using the combinatorial high-throughput materials exploration system "M-ist Combi" based on electrostatic spray deposition method. The merit of "M-ist Combi" system can prepare not only powder but also film library by changing applied voltage to the solution of starting materials. In the beginning, we prepared Li-Ni-Co-Ti oxides powder library for exploring the composition region with the single phase of layer-type compounds in short time. The obtained library was evaluated by the combinatorial X-ray powder diffractometor and established reaction phase diagrams. From the reaction phase diagrams, the new layered-type compounds were found wider composition region than the previous reported composition region of $LiNi_{0.8-x}Co_{0.2}Ti_xO_2$ ($0 \le x \le 0.1$). After obtaining information of reaction phase diagrams, the thin-film library layered-type Li-Ni-Co-Ti compounds was prepared by the "M-ist combi" system and evaluated charge-discharge property by the combinatorial electrode evaluation system.
By taking in these high-throughput screening process, the speed of materials exploration improve dramatically.

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MS35 O5

In-situ transmission electron microscopy investigation of orientation selected coalescence of nano-particles.

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The traditional theories divide the sintering roughly into two stages. In a first step, sintering necks between statistically oriented neighbouring particles are formed and rounded – the difference of capillary forces between particle and sintering neck results in a mass transport mainly along surfaces. Here, the porosity as well as distances between the centres of the grains remain unchanged. The driving force of the second stage of the sintering is the stepwise reduction of the surface energy by downsizing the pore-volume. Additional diffusion paths are along the grain boundaries as well as through the volume, the centres of the grains move towards each other, pores vanish. While the sintering processes for micro-crystalline grains can be described in this framework, the influence of lattice-misorientation between adjacent grains becomes important if nanoparticles are considered.
To study the sintering of nanoparticles, we did in-situ transmission electron microscopy experiments supported by simulations. For the simulations, a hybrid simulation technique combining kinetic Monte-Carlo (KMC) and classical molecular dynamics (MD) methods is used.
In-situ transmission electron microscopy (TEM) at elevated temperatures was used to obtain insights into the sintering behaviour of loose aggregates of oxide particles. The starting material was a self-supporting film consisting of nano-particles with a diameter of approximately 10 – 20

nm. No changes in the morphology were observed up to a temperature of 650 °C. Above 650 °C, the temperature was high enough to allow rotational movements. Single particles started to dither or vibrate. Possible reorientations of adjacent particles are the consequence. This observation is in good agreement with the simulations, which show that particles reorient before they grow together. Rather rotational than translational reorientation movements are observed. This process was simulated for different relative misorientations and particle sizes.

Thus, we show by simulation and experiment that nanoparticle sintering is at least three-step-process: First, the nanoparticles bring themselves into a favourable position. They do this by rotational movements. Second, the particles merge. The result is either a single crystalline piece which still has the shape of the two former particles or two particles separated by a crystallographic defined coincidence lattice. Third, the shape of the newly formed particle is optimized towards its equilibrium shape, which is spherical for single crystalline particles and dumbbell-like for particles separated by a coincidence lattice – the shape of the dumbbell depends on the energy of interface. Constellations with a completely suppressed sintering were found, both, in the simulation as well as in experiment, for some coincidence lattices.